

What is claimed is:

1. A hybrid inorganic/organic material comprising a polymerized scaffolding nanocomposite (PSN), wherein the nanocomposite contains a scaffolding functionality capable of chemically interacting with a surface of a second material.
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2. The hybrid material of claim 1, wherein the second material is a containment vessel.
3. The hybrid material of claim 1, wherein the scaffolding functionality is selected from the group consisting of vinyl, acrylate, methacrylate, acrylamide, methacrylamide, styrene, divinylbenzene, itaconate, fumarate, alkyne, and combinations thereof.
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4. The hybrid material of claim 1, wherein the surface of the second material is derivatized with an anchoring functionality.
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5. The hybrid material of claim 4, wherein the anchoring functionality is selected from the group consisting of vinyl, acrylate, methacrylate, acrylamide, methacrylamide, styrene, divinylbenzene, itaconate, fumarate, alkyne, azo compounds, and combinations thereof.
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6. The hybrid material of claim 4, wherein the scaffolding functionality and the anchoring functionality are copolymerizable.
7. The hybrid material of claim 2, wherein the containment vessel is selected from the group consisting of a capillary column, a glass lined steel column, a radial compression column, a trap column, a microfluidic device, a microchip, a sensor, an electronic circuit, a miniaturized SPE device, and an on-column frit.
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8. The hybrid material of claim 2, wherein the containment vessel is a fused silica capillary column.
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9. The hybrid material of claim 1, wherein the chemical interaction is formation of a covalent bond.
10. The hybrid material of claim 9, wherein the covalent bond is formed by
5 polymerization.
11. The hybrid material of claim 10, wherein the polymerization is initiated with a radical initiator.
- 10 12. The hybrid material of claim 11, wherein the radical initiator is minimally water soluble.
13. The hybrid material of claim 11, wherein the initiator is selected from the group consisting of 2,2'-azobis(isobutyronitrile), 2,2'-azobis(2-methylpropionamidine)
15 dihydrochloride, 4,4'-azobis(4-cyanovaleric acid), potassium persulfate, and peracetic acid.
14. The hybrid material of claim 1, wherein the inorganic portion of the hybrid material is a material selected from the group consisting of alumina, silica, titanium
20 oxide, zirconium oxide, and ceramic material.
15. The hybrid material of claim 1, wherein the inorganic portion of the hybrid material is silica.
- 25 16. The hybrid material of claim 1, wherein the PSN is the product of a reaction of an organosilane and an inorganic silane monomer.
17. The hybrid material of claim 16, wherein the PSN is the product of a reaction of a tetraalkoxysilane and an organosilane containing at least one polymerizable group.
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18. The hybrid material of claim 17, wherein said tetraalkoxysilane has the formula $\text{Si}(\text{OR}^1)_4$, where R^1 is a C_1 - C_3 alkyl moiety.
19. The hybrid material of claim 17, wherein said organosilane is an
5 organoalkoxysilane having the formula $\text{R}^2\text{Si}(\text{OR}^1)_3$ or $\text{R}^6[\text{Si}(\text{OR}^1)_3]_m$ where R^2 is a styryl, vinyl, an acrylate, methacrylate, acrylamide, methacrylamide, divinylbenzene, itaconate, fumarate, substituted or unsubstituted C_1 - C_{18} alkenylene, alkynylene or arylene, or a combination thereof; R^1 is a C_1 - C_4 alkyl moiety; R^6 is a substituted or unsubstituted C_1 - C_{18} alkenylene, alkynylene or arylene moiety bridging two or more
10 silicon atoms; and m is an integer greater than or equal to two.
20. The hybrid material of claim 19 wherein R^2 is vinyl, methacryloxypropyl, methacrylamidepropyl, or styrylethyl and R^1 is methyl or ethyl; or R^6 is a bridging N,N-bis(propylene) acrylamide group, $m = 2$, and R^1 is ethyl or methyl.
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21. The hybrid material of claim 17, wherein the organosilane is minimally water soluble.
22. The hybrid material of claim 17 wherein said tetraalkoxysilane is selected from
20 the group consisting of tetramethoxysilane and tetraethoxysilane.
23. The hybrid material of claim 17, wherein the tetraalkoxysilane is tetramethoxysilane.
24. The hybrid material of claim 17, wherein the polymerizable group is 3-methacryloxypropyl.
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25. The hybrid material of claim 17, wherein the polymerizable group is styrylethyl.
26. The hybrid material of claim 17, wherein the tetraalkoxysilane is minimally water soluble.
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27. The hybrid material of claim 17, wherein the organosilane is (3-methacryloxypropyl)trimethoxysilane.
28. The hybrid material of claim 1, wherein said pore structure of said hybrid material is modified by further including a surfactant or combination of different surfactants in said reaction, and by subjecting said material to hydrothermal treatment.
29. The hybrid material of claim 28, wherein said surfactant or combination of surfactants are nonionic surfactants.
30. The hybrid material of claim 29, wherein the surfactants are selected from the group consisting of surfactants comprised of block copolymers of polyethylene glycol and polypropyleneglycol, surfactants comprised of alkylphenoxypolyethoxyethanol, and polyethyleneglycol.
31. The hybrid material of claim 29, wherein the surfactant is Pluronic F38,
32. The hybrid material of claim 28, wherein said surfactant or combination of surfactants are selected from surfactants with a hydrophile-lipophile balance ranging from about 0 to 60.
33. The hybrid material of claim 28, wherein said surfactant or combination of surfactants are selected from surfactants with a hydrophile-lipophile balance ranging from about 10 to 50.
34. The hybrid material of claim 28, wherein said surfactant or combination of surfactants are selected from surfactants with a hydrophile-lipophile balance ranging from about 20 to 40.
35. The hybrid material of claim 28, wherein said surfactant or combination of surfactants are selected from surfactants with a hydrophile-lipophile balance ranging from about 30 to 40.

36. The hybrid material of claim 28, wherein said surfactant or combination of surfactants are selected from surfactants with a hydrophile-lipophile balance is about 33.
- 5 37. The hybrid material of claim 1, wherein said material has been surface modified by a surface modifier selected from the group consisting of an organic group surface modifier, a silanol group surface modifier, a polymeric coating surface modifier, and combinations thereof.
- 10 38. The hybrid material of claim 37, wherein said material has been surface modified by a polymeric coating surface modifier.
- 15 39. The hybrid material of claim 37, wherein said material has been surface modified by a combination of an organic group surface modifier and a silanol group surface modifier.
- 20 40. The hybrid material of claim 37, wherein said material has been surface modified by a combination of an organic group surface modifier and a polymeric coating surface modifier.
- 25 41. The hybrid material of claim 37, wherein said material has been surface modified by a combination of a silanol group surface modifier and a polymeric coating surface modifier.
- 30 42. The hybrid material of claim 37, wherein said material has been surface modified by a combination of an organic group surface modifier, a silanol group surface modifier, and a polymeric coating surface modifier.
43. The hybrid material of claim 37, wherein said material has been surface modified by a silanol group surface modifier.

44. The hybrid material of claim 37, wherein said material has been surface modified via formation of an organic covalent bond between an organic group of the material and a surface modifier.

5 45. The hybrid material of claim 37, wherein the surface modifier has the formula $Z_a(R')_b\text{Si-R}$, where $Z = \text{Cl, Br, I, C}_1 - \text{C}_5$ alkoxy, dialkylamino or trifluoromethanesulfonate; a and b are each an integer from 0 to 3 provided that $a + b = 3$; R' is a $\text{C}_1 - \text{C}_6$ straight, cyclic or branched alkyl group, and R is a functionalizing group.

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46. The hybrid material of claim 45 wherein R' is selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, t-butyl, sec-butyl, pentyl, isopentyl, hexyl and cyclohexyl.

15 47. The hybrid material of claim 45 wherein said functionalizing group R is a $\text{C}_1 - \text{C}_{30}$ alkyl group.

48. The hybrid material of claim 45 wherein said functionalizing group R is a $\text{C}_1 - \text{C}_{20}$ alkyl group.

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49. The hybrid material of claim 45 wherein said surface modifier is selected from the group consisting of octyltrichlorosilane, octadecyltrichlorosilane, octadecyldimethyl-N, N-dimethylaminosilane, octyldimethylchlorosilane, and octadecyldimethylchlorosilane.

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50. The hybrid material of claim 45, wherein said surface modifier is octadecyldimethyl-N, N-dimethylaminosilane.

30 51. The hybrid material of claim 45, wherein said functionalizing group R is selected from the group consisting of alkyl, alkenyl, alkynyl, aryl, cyano, amino, diol, nitro, ester, a cation or anion exchange group, an alkyl group containing an embedded polar functionality and an aryl group containing an embedded polar functionality.

52. A hybrid inorganic/organic monolith comprising a polymerized scaffolding nanocomposite (PSN), wherein the nanocomposite contains a scaffolding functionality capable of chemically interacting with a surface of a second material.
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53. The hybrid inorganic/organic monolith of claim 52, wherein the monolith is a capillary monolith.
54. The hybrid inorganic/organic monolith of claim 53, wherein the monolith has improved properties selected from the group consisting of enhanced wall adhesion and increased resistance to shrinkage.
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55. The hybrid inorganic/organic monolith of claim 54, wherein the enhanced wall adhesion is the result of chemical interaction between the scaffolding functionality of the polymer and an anchoring functionality on the surface of the second material.
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56. The hybrid inorganic/organic monolith of claim 52, wherein the second material is a containment vessel.
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57. The hybrid inorganic/organic monolith of claim 52, wherein the scaffolding functionality is selected from the group consisting of vinyl, acrylate, methacrylate, acrylamide, methacrylamide, styrene, divinylbenzene, itaconate, fumarate, alkyne, and combinations thereof.
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58. The hybrid inorganic/organic monolith of claim 52, wherein the surface of the second material is derivatized with an anchoring functionality.
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59. The hybrid inorganic/organic monolith of claim 58, wherein the anchoring functionality is selected from the group consisting of vinyl, acrylate, methacrylate, acrylamide, methacrylamide, styrene, divinylbenzene, itaconate, fumarate, alkyne, azo compounds, and combinations thereof.

60. The hybrid inorganic/organic monolith of claim 58, wherein the scaffolding functionality and the anchoring functionality are copolymerizable.
- 5 61. The hybrid inorganic/organic monolith of claim 56, wherein the containment vessel is selected from the group consisting of a capillary column, a glass lined steel column, a radial compression column, a trap column, a microfluidic device, a microchip, a sensor, a electronic circuit, a miniaturized SPE device, and an on-column frit.
- 10 62. The hybrid inorganic/organic monolith of claim 56, wherein the containment vessel is a fused silica capillary column.
63. The hybrid inorganic/organic monolith of claim 52, wherein the chemical interaction is formation of a covalent bond.
- 15 64. The hybrid inorganic/organic monolith of claim 63, wherein the covalent bond is formed by polymerization.
65. The hybrid inorganic/organic monolith of claim 64, wherein the polymerization is initiated with a radical initiator.
- 20 66. The hybrid inorganic/organic monolith of claim 65, wherein the radical initiator is minimally water soluble.
- 25 67. The hybrid inorganic/organic monolith of claim 65, wherein the initiator is selected from the group consisting of 2,2'-azobis(isobutyronitrile), 2,2'-azobis(2-methylpropionamidine) dihydrochloride, 4,4'-azobis(4-cyanovaleric acid), potassium persulfate, and peracetic acid.
- 30 68. The hybrid inorganic/organic monolith of claim 52, wherein the inorganic portion of the hybrid material is a material selected from the group consisting of alumina, silica, titanium oxide, zirconium oxide, and ceramic material.

69. The hybrid inorganic/organic monolith of claim 52, wherein the inorganic portion of the hybrid material is silica.

70. The hybrid inorganic/organic monolith of claim 52, wherein the PSN is the product of a reaction of an organosilane and an inorganic silane monomer.

71. The hybrid inorganic/organic monolith of claim 70, wherein the PSN is the product of a reaction of a tetraalkoxysilane and an organosilane containing at least one polymerizable group.

72. The hybrid inorganic/organic monolith of claim 71, wherein said tetraalkoxysilane has the formula $\text{Si}(\text{OR}^1)_4$, where R^1 is a $\text{C}_1 - \text{C}_3$ alkyl moiety.

73. The hybrid inorganic/organic monolith of claim 71, wherein said organosilane is an organoalkoxysilane having the formula $\text{R}^2\text{Si}(\text{OR}^1)_3$ or $\text{R}^6[\text{Si}(\text{OR}^1)_3]_m$ where R^2 is a styryl, vinyl, an acrylate, methacrylate, acrylamide, methacrylamide, divinylbenzene, itaconate, fumarate, substituted or unsubstituted $\text{C}_1 - \text{C}_{18}$ alkenylene, alkynylene or arylene, or a combination thereof; R^1 is a $\text{C}_1 - \text{C}_4$ alkyl moiety; R^6 is a substituted or unsubstituted $\text{C}_1 - \text{C}_{18}$ alkenylene, alkynylene or arylene moiety bridging two or more silicon atoms; and m is an integer greater than or equal to two.

74. The hybrid inorganic/organic monolith of claim 73 wherein R^2 is vinyl, methacryloxypropyl, methacrylamidepropyl, or styrylethyl and R^1 is methyl or ethyl; or R^6 is a bridging N,N-bis(propylene)acrylamide group, $m = 2$, and R^1 is ethyl or methyl.

75. The hybrid inorganic/organic monolith of claim 71, wherein the organosilane is minimally water soluble.

76. The hybrid inorganic/organic monolith of claim 71, wherein said tetraalkoxysilane is selected from the group consisting of tetramethoxysilane and tetraethoxysilane.

77. The hybrid inorganic/organic monolith of claim 71, wherein the tetraalkoxysilane is tetramethoxysilane.
- 5 78. The hybrid inorganic/organic monolith of claim 71, wherein the polymerizable group is 3-methacryloxypropyl.
79. The hybrid inorganic/organic monolith of claim 71, wherein the polymerizable group is styrylethyl.
- 10 80. The hybrid inorganic/organic monolith of claim 71, wherein the tetraalkoxysilane is minimally water soluble.
81. The hybrid inorganic/organic monolith of claim 71, wherein the organosilane is (3-methacryloxypropyl)trimethoxysilane.
- 15 82. The hybrid inorganic/organic monolith of claim 52, wherein said pore structure of said hybrid monolith is modified by further including a surfactant or combination of different surfactants in said reaction, and by subjecting said monolith to hydrothermal treatment.
- 20 83. The hybrid inorganic/organic monolith of claim 82, wherein said surfactant or combination of surfactants are nonionic surfactants.
- 25 84. The hybrid inorganic/organic monolith of claim 82, wherein the surfactants are selected from the group consisting of surfactants comprised of block copolymers of polyethylene glycol and polypropyleneglycol, surfactants comprised of alkylphenoxypolyethoxyethanol, and polyethyleneglycol.
- 30 85. The hybrid inorganic/organic monolith of claim 83, wherein the surfactant is Pluronic F38.

86. The hybrid inorganic/organic monolith of claim 82, wherein said surfactant or combination of surfactants are selected from surfactants with a hydrophile-lipophile balance ranging from about 0 to 60.

5 87. The hybrid inorganic/organic monolith of claim 82, wherein said surfactant or combination of surfactants are selected from surfactants with a hydrophile-lipophile balance ranging from about 10 to 50.

10 88. The hybrid inorganic/organic monolith of claim 82, wherein said surfactant or combination of surfactants are selected from surfactants with a hydrophile-lipophile balance ranging from about 20 to 40.

15 89. The hybrid inorganic/organic monolith of claim 82, wherein said surfactant or combination of surfactants are selected from surfactants with a hydrophile-lipophile balance ranging from about 30 to 40.

20 90. The hybrid inorganic/organic monolith of claim 82, wherein said surfactant or combination of surfactants are selected from surfactants with a hydrophile-lipophile balance is about 33.

25 91. The hybrid inorganic/organic monolith of claim 52, wherein said material has been surface modified by a surface modifier selected from the group consisting of an organic group surface modifier, a silanol group surface modifier, a polymeric coating surface modifier, and combinations thereof.

92. The hybrid inorganic/organic monolith of claim 91, wherein said material has been surface modified by a polymeric coating surface modifier.

30 93. The hybrid inorganic/organic monolith of claim 91, wherein said material has been surface modified by a combination of an organic group surface modifier and a silanol group surface modifier.

94. The hybrid inorganic/organic monolith of claim 91, wherein said material have been surface modified by a combination of an organic group surface modifier and a polymeric coating surface modifier.
- 5 95. The hybrid inorganic/organic monolith of claim 91, wherein said material has been surface modified by a combination of a silanol group surface modifier and a polymeric coating surface modifier.
- 10 96. The hybrid inorganic/organic monolith of claim 91, wherein said material has been surface modified by a combination of an organic group surface modifier, a silanol group surface modifier, and a polymeric coating surface modifier.
- 15 97. The hybrid inorganic/organic monolith of claim 91, wherein said material has been surface modified by a silanol group surface modifier.
98. The hybrid inorganic/organic monolith of claim 91, wherein said material has been surface modified via formation of an organic covalent bond between an organic group of the material and a surface modifier.
- 20 99. The hybrid inorganic/organic monolith of claim 91, wherein the surface modifier has the formula $Z_a(R')_b\text{Si-R}$, where $Z = \text{Cl, Br, I, C}_1 - \text{C}_5 \text{ alkoxy, dialkylamino or trifluoromethanesulfonate}$; a and b are each an integer from 0 to 3 provided that $a + b = 3$; R' is a $\text{C}_1 - \text{C}_6$ straight, cyclic or branched alkyl group, and R is a functionalizing group.
- 25 100. The hybrid inorganic/organic monolith of claim 99 wherein R' is selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, t-butyl, sec-butyl, pentyl, isopentyl, hexyl and cyclohexyl.
- 30 101. The hybrid inorganic/organic monolith of claim 99 wherein said functionalizing group R is a $\text{C}_1 - \text{C}_{30}$ alkyl group.

102. The hybrid inorganic/organic monolith of claim 99 wherein said functionalizing group R is a C₁ – C₂₀ alkyl group.
103. The hybrid inorganic/organic monolith of claim 99 wherein said surface modifier is selected from the group consisting of octyltrichlorosilane, octadecyltrichlorosilane, octadecyldimethyl-N, N-dimethylaminosilane, octyldimethylchlorosilane, and octadecyldimethylchlorosilane.
104. The hybrid inorganic/organic monolith of claim 99, wherein said surface modifier is octadecyldimethyl-N, N-dimethylaminosilane.
105. The hybrid inorganic/organic monolith of claim 99, wherein said functionalizing group R is selected from the group consisting of alkyl, alkenyl, alkynyl, aryl, cyano, amino, diol, nitro, ester, a cation or anion exchange group, or an alkyl or aryl group containing an embedded polar functionality.
106. A method of preparation of a hybrid inorganic/organic monolith comprising a polymerized scaffolding nanocomposite (PSN), wherein the nanocomposite contains a scaffolding functionality capable of chemically interacting with a surface of a second material, said method comprising the steps of
- a) forming a sol-gel by the reaction of two or more monomers;
 - b) initiating a polymerization reaction; and
 - c) allowing the monomers to react through a polymerization sol-gel (PSG) reaction,
- thereby preparing the hybrid inorganic/organic monolith.
107. A method of preparation of a hybrid inorganic/organic monolith comprising a polymerized scaffolding nanocomposite (PSN), wherein the nanocomposite contains a scaffolding functionality capable of chemically interacting with a surface of a second material, said method comprising the steps of
- a) forming a sol-gel by the reaction of two or more monomers;
 - b) initiating a polymerization reaction;

c) allowing the monomers to react through a polymerization sol-gel (PSG) reaction; and

d) modifying the pore structure of the material,
thereby preparing the hybrid inorganic/organic monolith.

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108. The method of claim 106 or 107, wherein the sol-gel reaction is acid catalyzed.

109. The method of claim 108, wherein the acid is acetic acid.

10 110. The method of claim 106 or 107, wherein the sol-gel reaction is performed at a temperature ranging from about 0 °C to about room temperature.

111. The method of claim 110, wherein the sol-gel reaction is performed at a temperature of about 0 °C.

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112. The method of claim 110, wherein the sol-gel reaction is performed at room temperature.

113. The method of claim 106 and 107, wherein the sol-gel reaction is performed at
20 low pH.

114. The method of claim 113, wherein the sol-gel reaction is performed at about pH 2-3.

25 115. The method of claim 106 or 107, wherein the sol-gel reaction occurs in the presence of urea.

116. The method of claim 106 or 107, wherein the polymerization is initiated with a radical initiator.

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117. The method of claim 116, wherein the polymerization is initiated with a radical initiator at increased temperature.

5 118. The method of claim 117, wherein the increased temperature is above room temperature.

119. The method of claim 118, wherein the increased temperature is about 60-65°C.

10 120. The method of claim 116, wherein the radical initiator is minimally water soluble.

15 121. The method of claim 116, wherein the initiator is selected from the group consisting of 2,2'-azobis(isobutyronitrile), 2,2'-azobis(2-methylpropionamidine) dihydrochloride, 4,4'-azobis(4-cyanovaleric acid), potassium persulfate, and peracetic acid.

122. The method of claim 106 and 107, wherein the PSG reaction is performed at temperature sufficient to achieve simultaneous polymerization and sol gel reactions.

20 123. The method of claim 122, wherein the PSG reaction is performed at 65 °C.

124. The method of claim 122, wherein the PSG reaction is performed for an amount of time sufficient to prepare the hybrid inorganic/organic monolith.

25 125. The method of claim 106 or 107, wherein the second material is a containment vessel with a surface capable of receiving the PSN material.
a derivatized with an anchoring functionality.

30 126. The method of claim 106 or 107, wherein the surface of the second material is derivatized with an anchoring functionality.

127. The method of claim 126, wherein the scaffolding functionality and the anchoring functionality are copolymerizable.
- 5 128. The method of claim 125, where the containment vessel is selected from the group consisting of a capillary column, a glass lined steel column, a radial compression column, a trap column, a microfluidic device, a microchip, a sensor, an electronic circuit, a miniaturized SPE device, and an on-column frit.
129. The method of claim 128, wherein the containment vessel is a capillary column.
- 10 130. The method of claim 129, where the containment vessel is a fused silica capillary column.
131. The method of claim 106 or 107, wherein the chemical interaction is formation of a covalent bond.
- 15 132. The method of claim 131, wherein the covalent bond is formed by copolymerization.
- 20 133. The method of claim 106 or 107, wherein the PSN is the product of a reaction of an organosilane and an inorganic silane monomer.
134. The method of claim 133, wherein the PSN is the product of a reaction of a tetraalkoxysilane and an organosilane containing at least one polymerizable group.
- 25 135. The method of claim 134, wherein said tetraalkoxysilane has the formula $\text{Si}(\text{OR}^1)_4$, where R^1 is a $\text{C}_1 - \text{C}_3$ alkyl moiety.
- 30 136. The method of claim 134, wherein said organosilane is an organoalkoxysilane having the formula $\text{R}^2\text{Si}(\text{OR}^1)_3$ or $\text{R}^6[\text{Si}(\text{OR}^1)_3]_m$ where R^2 is a styryl, vinyl, an acrylate, methacrylate, acrylamide, methacrylamide, divinylbenzene, itaconate, fumarate, substituted or unsubstituted $\text{C}_1 - \text{C}_{18}$ alkenylene, alkynylene or arylene, or a combination

thereof; R^1 is a $C_1 - C_4$ alkyl moiety; R^6 is a substituted or unsubstituted $C_1 - C_{18}$ alkenylene, alkynylene or arylene moiety bridging two or more silicon atoms; and m is an integer greater than or equal to two.

5 137. The method of claim 136 wherein R^2 is vinyl, methacryloxypropyl, methacrylamidepropyl, or styrylethyl and R^1 is methyl or ethyl; or R^6 is a bridging N,N-bis(propylene)acrylamide group, $m = 2$, and R^1 is ethyl or methyl.

10 138. The method of claim 133, wherein the organosilane is minimally water soluble.

139. The method of claim 134 wherein said tetraalkoxysilane is selected from the group consisting of tetramethoxysilane and tetraethoxysilane.

15 140. The method of claim 134, wherein the tetraalkoxysilane is tetramethoxysilane.

141. The method of claim 134, wherein the polymerizable group is 3-methacryloxypropyl.

20 142. The method of claim 134, wherein the polymerizable group is styrylethyl.

143. The method of claim 134, wherein the tetraalkoxysilane is minimally water soluble.

25 144. The method of claim 134, wherein the organosilane is (3-methacryloxypropyl)trimethoxysilane.

30 145. The method of claim 133, wherein the organosilane is (3-methacryloxypropyl)trimethoxysilane and the inorganic silane monomer is tetramethoxysilane.

146. The method of claim 145, wherein the (3-methacryloxypropyl)trimethoxysilane and the tetramethoxysilane are present in a volume to volume ratio of 1 to 4.

147. The method of claim 106 or 107, wherein said method further comprises surface
5 modifying said monolith.

148. The method of claim 147, wherein said monolith has been surface modified by a surface modifier selected from the group consisting of an organic group surface modifier, a silanol group surface modifier, a polymeric coating surface modifier, and
10 combinations thereof.

149. The method of claim 148, wherein said material has been surface modified by a polymeric coating surface modifier.

150. The method of claim 148, wherein said material has been surface modified by a combination of an organic group surface modifier and a silanol group surface modifier.
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151. The method of claim 148, wherein said material have been surface modified by a combination of an organic group surface modifier and a polymeric coating surface
20 modifier.

152. The method of claim 148, wherein said material has been surface modified by a combination of a silanol group surface modifier and a polymeric coating surface
25 modifier.

153. The method of claim 148, wherein said material has been surface modified by a combination of an organic group surface modifier, a silanol group surface modifier, and a polymeric coating surface modifier.

154. The method of claim 148, wherein said material has been surface modified by a silanol group surface modifier.
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155. The method of claim 148, wherein said material has been surface modified via formation of an organic covalent bond between an organic group of the material and a surface modifier.
- 5 156. The method of claim 106 or 107 wherein said pore structure of said monolith is modified by further including a surfactant or combination of different surfactants in said reaction, and by subjecting said monolith to hydrothermal treatment.
- 10 157. The method of claim 156 wherein said surfactant or combination of surfactants are nonionic surfactants.
158. The method of claim 156 wherein said monolith is modified by further including a surfactant.
- 15 159. The method of claim 157, wherein the surfactants are selected from the group consisting of surfactants comprised of block copolymers of polyethylene glycol and polypropyleneglycol, surfactants comprised of alkylphenoxypolyethoxyethanol, and polyethyleneglycol.
- 20 160. The method of claim 157, wherein the surfactant is Pluronic F38,
161. The method of claim 156 wherein said surfactant or combination of surfactants are selected from surfactants with a hydrophile-lipophile balance ranging from about 0 to 60.
- 25 162. The method of claim 156 wherein said surfactant or combination of surfactants are selected from surfactants with a hydrophile-lipophile balance ranging from about 10 to 50.
- 30 163. The method of claim 156 wherein said surfactant or combination of surfactants are selected from surfactants with a hydrophile-lipophile balance ranging from about 20 to 40.

164. The method of claim 156 wherein said surfactant or combination of surfactants are selected from surfactants with a hydrophile-lipophile balance ranging from about 30 to 40.

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165. The method of claim 156 wherein said surfactant or combination of surfactants are selected from surfactants with a hydrophile-lipophile balance is about 33.

166. The method of claim 156, wherein the hydrothermal treatment comprises
10 subjecting the material to a temperature of 60-200 °C.

167. The method of claim 156, wherein the hydrothermal treatment comprises
subjecting the material to a temperature of 65-125 °C.

15 168. The method of claim 167, wherein the temperature is 120 °C.

169. The method of claim 158, wherein the pore structure is modified by
hydrothermal treatment comprising further condensation of the siloxane network formed
during the PSG reaction, and dissolution and redeposition of silicic acid silicates from
20 and to the surface of the pore structure.

170. The method of claim 169, wherein the condensation is base catalyzed.

171. The method of claim 170, wherein the base is ammonia.

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172. The method of claim 171, wherein the ammonia is generated by high temperature
decomposition of urea.

173. The method of claim 147, wherein the surface modification step includes surface
30 modifying said monolith with a surface modifier having the formula $Z_a(R')_b\text{Si-R}$, where
 $Z = \text{Cl, Br, I, C}_1 - \text{C}_5 \text{ alkoxy, dialkylamino or trifluoromethanesulfonate}$; a and b are each

an integer from 0 to 3 provided that $a + b = 3$; R' is a $C_1 - C_6$ straight, cyclic or branched alkyl group, and R is a functionalizing group.

5 174. The method of claim 173 wherein R' is selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, t-butyl, sec-butyl, pentyl, isopentyl, hexyl and cyclohexyl.

175. The method of claim 173 wherein said functionalizing group R is a $C_1 - C_{30}$ alkyl group.

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176. The method of claim 173 wherein said functionalizing group R is a $C_1 - C_{20}$ alkyl group.

15 177. The method of claim 173 wherein said functionalizing group R is a $C_1 - C_{10}$ alkyl group.

178. The method of claim 173 wherein said surface modifier is selected from the group consisting of octyltrichlorosilane, octadecyltrichlorosilane, octyldimethylchlorosilane, octadecyldimethyl-N,N-dimethylaminosilane, and
20 octadecyldimethylchlorosilane.

179. The method of claim 178 wherein said surface modifier is octadecyldimethyl-N,N-dimethylaminosilane.

25 180. The method of claim 173, wherein said functionalizing group R is selected from the group consisting of alkyl, alkenyl, alkynyl, aryl, cyano, amino, diol, nitro, ester, a cation or anion exchange group, or an alkyl or aryl group containing an embedded polar functionality.

30 181. The method of claim 147 wherein any free silanol groups remaining from said surface modification procedure are endcapped.

182. A separations device comprising
- a) a surface capable of accepting a monolith material comprising a polymerized scaffolding nanocomposite (PSN) material, said surface comprising an anchoring functionality and
 - 5 b) a hybrid inorganic/organic monolith comprising a polymerized scaffolding nanocomposite (PSN), wherein the nanocomposite contains a scaffolding functionality capable of chemically interacting with the anchoring functionality on said surface, and wherein said hybrid organic/inorganic monolith is anchored to said surface by a chemical interaction between said scaffolding functionality and anchoring
 - 10 functionality.
183. The separations device of claim 182, wherein said device is selected from the group consisting of chromatographic columns, thin layer plates, filtration membranes, sample cleanup devices, and microtiter plates.
- 15
184. The separations device of claim 182, wherein said device is a chromatographic column.
185. The separations device of claim 184, wherein the chromatographic column has an
- 20 inner diameter (I.D.) greater than 50 μm .
186. The separations device of claim 184, wherein the chromatographic column has an I.D. greater than of 100 μm .
- 25
187. The separations device of claim 184, wherein the chromatographic column has an I.D. greater than of 150 μm .
188. The separations device of claim 184, wherein the chromatographic column has an I.D. greater than of 200 μm .
- 30
189. The separations device of claim 184, wherein the chromatographic column has an I.D. greater than of 250 μm .

190. The separations device of claim 184, wherein said device is a capillary column.
191. The separations device of claim 184 wherein said device is a fused-inorganic
5 capillary column, wherein the inorganic portion is selected from the group consisting of silica, alumina, zirconium oxide, titanium oxide, ceramics, tin oxide, and combinations thereof.
192. The separations device of claim 182 wherein the monolith has improved
10 properties selected from the group consisting of enhanced wall adhesion and increased resistance to shrinkage.
193. The separations device of claim 192, wherein the enhanced wall adhesion is the
15 result of chemical interaction between the scaffolding functionality of the polymer and the anchoring functionality of the wall of the containment vessel.
194. A fused-silica capillary column, comprising
- a) a fused-silica capillary column having a cylindrical interior surface
capable of accepting a monolith comprising a polymerized scaffolding nanocomposite
20 (PSN) material, said interior surface comprising an anchoring functionality, and
- b) a hybrid inorganic/organic monolith comprising a polymerized
scaffolding nanocomposite (PSN), wherein the nanocomposite contains a scaffolding
functionality capable of chemically interacting with the anchoring functionality on said
surface, and wherein said hybrid organic/inorganic monolith is anchored to said surface
25 by a chemical interaction between said scaffolding functionality and anchoring
functionality.
195. The fused-silica capillary column of claim 194, wherein the capillary column has
an inner diameter (I.D.) greater than 50 μm .
- 30 196. The fused-silica capillary column of claim 194, wherein the capillary column has
an I.D. greater than of 100 μm .

197. The fused-silica capillary column of claim 194, wherein the capillary column has an I.D. greater than of 150 μm .
- 5 198. The fused-silica capillary column of claim 194, wherein the capillary column has an I.D. greater than of 200 μm .
199. The fused-silica capillary column of claim 194, wherein the capillary column has an I.D. greater than of 250 μm .
- 10 200. The fused-silica capillary column of claim 194, wherein the scaffolding functionality is selected from the group consisting of vinyl, acrylate, methacrylate, acrylamide, methacrylamide, styrene, divinylbenzene, itaconate, fumarate, alkyne, and combinations thereof.
- 15 201. The fused-silica capillary column of claim 194, wherein the anchoring functionality is selected from the group consisting of vinyl, acrylate, methacrylate, acrylamide, methacrylamide, styrene, divinylbenzene, itaconate, fumarate, alkyne, azo compounds, and combinations thereof.
- 20 202. The fused-silica capillary column of claim 194, wherein the scaffolding functionality and the anchoring functionality are copolymerizable.
- 25 203. The fused-silica capillary column of claim 194, wherein the chemical interaction is formation of a covalent bond.
204. The fused-silica capillary column of claim 203, wherein the covalent bond is formed by polymerization.
- 30 205. The fused-silica capillary column of claim 204, wherein the polymerization is initiated with a radical initiator.

206. The fused-silica capillary column of claim 205, wherein the radical initiator is minimally water soluble.
- 5 207. The fused-silica capillary column of claim 206, wherein the initiator is selected from the group consisting of 2,2'-azobis(isobutyronitrile), 2,2'-azobis(2-methylpropionamidine) dihydrochloride, 4,4'-azobis(4-cyanovaleric acid), potassium persulfate, and peracetic acid.
- 10 208. The fused-silica capillary column of claim 194, wherein the inorganic portion of the hybrid material is a material selected from the group consisting of alumina, silica, titanium oxide, zirconium oxide, and ceramic material.
- 15 209. The fused-silica capillary column of claim 194, wherein the inorganic portion of the hybrid material is silica.
210. The fused-silica capillary column of claim 194, wherein the PSN is the product of a reaction of an organosilane and an inorganic silane monomer.
- 20 211. The fused-silica capillary column of claim 210, wherein the PSN is the product of a reaction of a tetraalkoxysilane and an organosilane containing at least one polymerizable group.
- 25 212. The fused-silica capillary column of claim 211, wherein said tetraalkoxysilane has the formula $\text{Si}(\text{OR}^1)_4$, where R^1 is a $\text{C}_1 - \text{C}_3$ alkyl moiety.
- 30 213. The fused-silica capillary column of claim 211, wherein said organosilane is an organoalkoxysilane having the formula $\text{R}^2\text{Si}(\text{OR}^1)_3$ or $\text{R}^6[\text{Si}(\text{OR}^1)_3]_m$ where R^2 is a styryl, vinyl, an acrylate, methacrylate, acrylamide, methacrylamide, divinylbenzene, itaconate, fumarate, substituted or unsubstituted $\text{C}_1 - \text{C}_{18}$ alkenylene, alkynylene or arylene, or a combination thereof; R^1 is a $\text{C}_1 - \text{C}_4$ alkyl moiety; R^6 is a substituted or

unsubstituted C₁ - C₁₈ alkenylene, alkynylene or arylene moiety bridging two or more silicon atoms; and m is an integer greater than or equal to two.

214. The fused-silica capillary column of claim 213, wherein R² is vinyl,
5 methacryloxypropyl, methacrylamidepropyl, or styrylethyl and R¹ is methyl or ethyl; or R⁶ is a bridging N,N-bis(propylene)acrylamide group, m = 2, and R¹ is ethyl or methyl.

215. The fused-silica capillary column of claim 211, wherein the organosilane is minimally water soluble.

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216. The fused-silica capillary column of claim 211, wherein said tetraalkoxysilane is selected from the group consisting of tetramethoxysilane and tetraethoxysilane.

217. The fused-silica capillary column of claim 211, wherein the tetraalkoxysilane is
15 tetramethoxysilane.

218. The fused-silica capillary column of claim 211, wherein the polymerizable group is 3-methacryloxypropyl.

219. The fused-silica capillary column of claim 211, wherein the polymerizable group is styrylethyl.
20

220. The fused-silica capillary column of claim 211, wherein the tetraalkoxysilane is minimally water soluble.

25

221. The fused-silica capillary column of claim 211, wherein the organosilane is (3-methacryloxypropyl)trimethoxysilane.

222. The fused-silica capillary column of claim 194, wherein the pore structure of said
30 hybrid monolith is modified by further including a surfactant or combination of different surfactants in said reaction, and by subjecting said monolith to hydrothermal treatment.

223. The fused-silica capillary column of claim 222, wherein said surfactant or combination of surfactants are nonionic surfactants.
- 5 224. The fused-silica capillary column of claim 223, wherein the surfactants are selected from the group consisting of surfactants comprised of block copolymers of polyethylene glycol and polypropyleneglycol, surfactants comprised of alkylphenoxypolyethoxyethanol, and polyethyleneglycol.
- 10 225. The fused-silica capillary column of claim 223, wherein the surfactant is Pluronic F38,
226. The fused-silica capillary column of claim 222, wherein said surfactant or combination of surfactants are selected from surfactants with a hydrophile-lipophile
15 balance ranging from about 0 to 60.
227. The fused-silica capillary column of claim 222, wherein said surfactant or combination of surfactants are selected from surfactants with a hydrophile-lipophile balance ranging from about 10 to 50.
- 20 228. The fused-silica capillary column of claim 222, wherein said surfactant or combination of surfactants are selected from surfactants with a hydrophile-lipophile balance ranging from about 20 to 40.
- 25 229. The fused-silica capillary column of claim 222, wherein said surfactant or combination of surfactants are selected from surfactants with a hydrophile-lipophile balance ranging from about 30 to 40.
- 30 230. The fused-silica capillary column of claim 222, wherein said surfactant or combination of surfactants are selected from surfactants with a hydrophile-lipophile balance is about 33.

231. The fused-silica capillary column of claim 194, wherein said monolith has been surface modified by a surface modifier selected from the group consisting of an organic group surface modifier, a silanol group surface modifier, a polymeric coating surface modifier, and combinations thereof.

5

232. The fused-silica capillary column of claim 231, wherein said material has been surface modified by a polymeric coating surface modifier.

10 233. The fused-silica capillary column of claim 231, wherein said material has been surface modified by a combination of an organic group surface modifier and a silanol group surface modifier.

15 234. The fused-silica capillary column of claim 231, wherein said material have been surface modified by a combination of an organic group surface modifier and a polymeric coating surface modifier.

235. The fused-silica capillary column of claim 231, wherein said material has been surface modified by a combination of a silanol group surface modifier and a polymeric coating surface modifier.

20

236. The fused-silica capillary column of claim 231, wherein said material has been surface modified by a combination of an organic group surface modifier, a silanol group surface modifier, and a polymeric coating surface modifier.

25 237. The fused-silica capillary column of claim 231, wherein said material has been surface modified by a silanol group surface modifier.

30 238. The fused-silica capillary column of claim 231, wherein said material has been surface modified via formation of an organic covalent bond between an organic group of the material and a surface modifier.

239. The fused-silica capillary column of claim 231, wherein the surface modifier has the formula $Z_a(R')_bSi-R$, where $Z = Cl, Br, I, C_1 - C_5$ alkoxy, dialkylamino or trifluoromethanesulfonate; a and b are each an integer from 0 to 3 provided that $a + b = 3$; R' is a $C_1 - C_6$ straight, cyclic or branched alkyl group, and R is a functionalizing group.

240. The fused-silica capillary column of claim 239, wherein R' is selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, t-butyl, sec-butyl, pentyl, isopentyl, hexyl and cyclohexyl.

241. The fused-silica capillary column of claim 239, wherein said functionalizing group R is a $C_1 - C_{30}$ alkyl group.

242. The fused-silica capillary column of claim 239, wherein said functionalizing group R is a $C_1 - C_{20}$ alkyl group.

243. The fused-silica capillary column of claim 239, wherein said surface modifier is selected from the group consisting of octyltrichlorosilane, octadecyltrichlorosilane, octadecyldimethyl-N, N-dimethylaminosilane, octyldimethylchlorosilane, and octadecyldimethylchlorosilane.

244. The fused-silica capillary column of claim 239, wherein said surface modifier is octadecyldimethyl-N, N-dimethylaminosilane.

245. The fused-silica capillary column of claim 239, wherein said functionalizing group R is selected from the group consisting of alkyl, alkenyl, alkynyl, aryl, cyano, amino, diol, nitro, ester, a cation or anion exchange group, or an alkyl or aryl group containing an embedded polar functionality.

246. A method of *in situ* preparation of a hybrid inorganic/organic monolith in a fused-silica capillary column, said method comprising:

forming an anchoring functionality on an interior surface of said capillary column; and

5 forming inside said capillary column a hybrid inorganic/organic monolith comprising a polymerized scaffolding nanocomposite (PSN), wherein the nanocomposite contains a scaffolding functionality capable of chemically interacting with the anchoring functionality on said surface, said monolith being formed by:

- a) forming a sol-gel by the reaction of two or more monomers;
- b) initiating a polymerization reaction; and
- 10 c) allowing the monomers to react through a polymerization sol-gel (PSG) reaction;

whereby said scaffolding functionality and said anchoring functionality chemically interact to thereby anchor said monolith to said surface, such that a hybrid inorganic/organic monolith is prepared *in situ* in the fused-silica capillary column.

15 247. A method of *in situ* preparation of a hybrid inorganic/organic monolith in a fused-silica capillary column, said method comprising:

forming an anchoring functionality on an interior surface of said capillary column; and

20 forming inside said capillary column a hybrid inorganic/organic monolith comprising a polymerized scaffolding nanocomposite (PSN), wherein the nanocomposite contains a scaffolding functionality capable of chemically interacting with the anchoring functionality on said surface, said monolith being formed by:

- a) forming a sol-gel by the reaction of two or more monomers;
- b) initiating a polymerization reaction;
- 25 c) allowing the monomers to react through a polymerization sol-gel (PSG) reaction; and
- d) modifying the pore structure of the monolith,

whereby said scaffolding functionality and said anchoring functionality chemically interact to thereby anchor said monolith to said surface, such that a hybrid
30 inorganic/organic monolith is prepared *in situ* in the fused-silica capillary column.

248. An inorganic/organic hybrid monolith comprising a scaffolding functionality capable of chemically interacting with a surface of a second material, produced by the process of

- a) forming a sol-gel by the reaction of two or more monomers;
- 5 b) initiating a polymerization reaction; and
- c) allowing the monomers to react through a polymerization sol-gel (PSG) reaction.

249. An inorganic/organic hybrid monolith comprising a scaffolding functionality capable of chemically interacting with a surface of a second material, produced by the process of

- a) forming a sol-gel by the reaction of two or more monomers;
- b) initiating a polymerization reaction;
- c) allowing the monomers to react through a polymerization sol-gel (PSG) reaction; and
- 15 d) modifying the pore structure of the monolith.

250. A method of preparation of a hybrid inorganic/organic material comprising a polymerized scaffolding nanocomposite (PSN), comprising the steps of

- 20 a) forming a sol-gel by the reaction of two or more monomers;
- b) initiating a polymerization reaction; and
- c) allowing the monomers to react through a polymerization sol-gel (PSG) reaction,

thereby preparing the hybrid inorganic/organic material, wherein the material contains a scaffolding functionality capable of chemically interacting with a surface of a second material.

251. A method of preparation of a hybrid inorganic/organic material comprising a polymerized scaffolding nanocomposite (PSN), comprising the steps of

- 30 a) forming a sol-gel by the reaction of two or more monomers;
- b) initiating a polymerization reaction;

c) allowing the monomers to react through a polymerization sol-gel (PSG) reaction; and

- d) modifying the pore structure of the material,
- thereby preparing the hybrid inorganic/organic material, wherein the nanocomposite
- 5 contains a scaffolding functionality capable of chemically interacting with a surface of a second material.